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SOLUBILITIES OF SELECTED METALS IN MERCURY:

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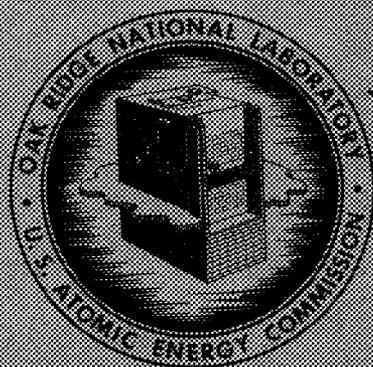
A. F. Messing
O. C. Dean

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CHEMICAL TECHNOLOGY DIVISION
Chemical Development Section B

SOLUBILITIES OF SELECTED METALS IN MERCURY:
HERMEX PROCESS

A. F. Messing
O. C. Dean

DATE ISSUED

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OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
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ABSTRACT

The solubilities of uranium, thorium, gadolinium, samarium, and neodymium in mercury were determined from room temperature to 356°C. Equations of the form $\log \text{ of solubility (wt \%)} = a + b/T$ were developed for these metals. Integral heats of solution were calculated for each.

The solubilities of ruthenium, palladium, zirconium, and molybdenum in mercury in the presence of excess uranium were also determined; however, the low solubility of zirconium and molybdenum gave solutions with a concentration below the limit of detection in the analytical method used, and therefore their values are reported as an upper solubility limit.

Uranium solubility in a 0.1 wt % magnesium amalgam was approximately 1.2-1.5 times greater than in mercury alone. When uranium and thorium were present in the same mercury solution, their solubilities were mutually depressed.

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1.0 INTRODUCTION

The purpose of this investigation was to determine the solubilities in mercury of several metals, including uranium and thorium and some of the major fission products contained in irradiated uranium. A knowledge of these values is necessary in order to evaluate the feasibility of the Hermex process as a method of fuel processing.

In the Hermex process, irradiated uranium and alloys containing >90% uranium are decontaminated from fission products by extraction with mercury, recrystallization, and distillation. It has been proposed for metallic fuel processing,¹ and early evaluation studies, including a preliminary flowsheet,² have been reported. Studies on the use of mercury in the processing of plutonium-rich fuels are also being performed at the Los Alamos Scientific Laboratory.³

Data on the solubility of elements in mercury, with emphasis on actinide, fission product, and structural metals, is meager or completely lacking. Information obtainable is usually at one or two temperatures or over a very small temperature range, usually below 100°C.^{3-8,13-16} Frequently, results reported by two different investigators on the solubility of the same metal at the same temperature differ by as much as a factor of 10^3 or greater. No doubt some or all of this disagreement is due to one or more of the difficulties encountered in mercury solubility determinations discussed below.

Many unusual difficulties are encountered in the determination of the solubilities of metals in mercury. One of the most common is the extreme reactivity of amalgams to air or water, including pyrophoricity. Low values may be obtained on approaching saturation from below because of the slow attack of mercury on unwetted surfaces at lower temperatures. On the other hand, high values may result on approaching saturation from above because of the tendency of amalgams to form nearly colloidal dispersions on cooling.⁹

In this study the solubilities in mercury of the actinide metals uranium and thorium and the rare earth representatives gadolinium, samarium, and neodymium were determined from 25 to 356°C. The solubilities of several of the more noble metals, ruthenium, palladium, molybdenum, and zirconium, in mercury saturated with uranium were also determined. Solubility determinations should also be made on other important fission product metals not included in this report.

The authors are indebted to G. R. Wilson, G. W. Leddicotte, and P. F. Thomason and staffs of the ORNL Analytical Chemistry Division and to H. R. Guinn and staff of the Special Testing Laboratory for analyses performed. Acknowledgment is also made to E. R. Johns who performed much of the laboratory work.

2.0 RESULTS AND DISCUSSION

2.1 Solubility of Actinide Metals in Mercury

By the method of least squares^{10,11} an equation of the form $\log C = a + b/T$ was fitted to the observed solubility data for uranium (Table 2.1) and thorium (Table 2.2), where C is the metal solubility in weight percent, T is the temperature in degrees Kelvin, and a and b are constants. The derived equations and their estimated standard deviations in log C are

$$\log \text{ of uranium solubility (wt \%)} = 2.33213 - 1418.83/T, \sigma_{\text{fit}} = 0.01536$$

and

$$\log \text{ of thorium solubility (wt \%)} = 0.426493 - 698.472/T, \sigma_{\text{fit}} = 0.02046$$

From these equations, the solubility of uranium was determined to be 0.00661 wt % at 40°C and 1.19 wt % at 356°C (Table 2.1, Fig. 2.1). Thorium solubility in the same temperature range is 0.00222 to 0.0290 wt % (Table 2.2, Fig. 2.1).

Integral heats of solution for the two metals in mercury are 6.49 kcal per mole of uranium and 2.93 kcal per mole of thorium. These values and those for the rare earths (Sect. 2.3) were calculated from the equation

$$\Delta H_{\text{sol}} = \frac{R \ln N_2/N_1}{1/T_1 - 1/T_2}$$

as developed by Glasstone,¹² where N is the mole fraction of the solute, T is the absolute temperature, and R is the gas constant. The solubility of plutonium in mercury determined by Bowersox and Leary¹³ is included in Fig. 2.1 for direct reference and comparison.

These results are supported by the uranium solubility data of Wilson, Ahmann, and Baldwin¹⁴ and the room temperature solubility value for thorium of Strachan and Harris.⁷ On the other hand, the uranium solubility reported by Frost¹⁵ and the thorium solubility reported by the workers at Armour Research Foundation¹⁶ are considerably different, one order and two orders greater, respectively. The reason for this large discrepancy is unknown, but it appears that the electrical resistivity method used by Frost and the Armour workers is subject to error in mercury solutions.¹⁷

The data of only a single run are included for both uranium and thorium. When their solubilities were determined in conjunction with other experiments, the results were identical to those shown in Fig. 2.1, within

Table 2.1 Solubility of Uranium in Mercury

Temperature, °C	Reciprocal Temperature, 10 ³ /°K	Solubility, wt %	
		Observed	Calculated ^a
356	1.59	1.18	1.19
356	1.59	1.24	1.19
250	1.91	0.454	0.418
250	1.91	0.419	0.418
150	2.37	0.0930	0.0932
100	2.68	0.0340	0.0338
50	3.09	0.0094	0.00916
50	3.09	0.0093	0.00916
40	3.19	0.0067	0.00661
70	2.91	0.0155	0.0155
145	2.39	0.0819	0.0873
145	2.39	0.0834	0.0873
205	2.09	0.230	0.240
205	2.09	0.238	0.240
300	1.74	0.730	0.729
300	1.74	0.725	0.729

^aFrom equation \log of uranium solubility (wt %) = $2.33213 - 1418.81/T$.

Table 2.2 Solubility of Thorium in Mercury

Temperature, °C	Reciprocal Temperature, 10 ³ /°K	Solubility, wt %	
		Observed	Calculated ^a
356	1.59	0.0295	0.0290
280	1.81	0.0203	0.0204
220	2.03	0.0151	0.0143
160	2.31	0.00921	0.00898
60	3.00	0.00313	0.00300
40	3.19	0.00211	0.00222
120	2.51	0.00675	0.00661
200	2.11	0.0120	0.0124
300	1.74	0.0235	0.0226

^aFrom equation \log of thorium solubility (wt %) = $-0.426493 - 698.472/T$.

experimental error. Initial solutions were prepared by boiling 50 g of uranium or 57 g of thorium in 200 ml of mercury. At the conclusion of a run the dissolver was disassembled and the residue inspected, and considerable metal quasi amalgam residue was present in both cases. The metals had been completely converted to their respective mercurides. The mercury-bright solution in the case of uranium indicated that no oxidation had occurred during the course of the experiment. Only the slightest trace of oxidation was evident for thorium.

In a 0.1 wt % magnesium amalgam, uranium solubility increased from 0.0056 wt % at 20°C to 1.41 wt % at 356°C (Table 2.3). This is an increase over the solubility of uranium in mercury of about 50% at room temperature and about 20% at 356°C. The initial mixture contained 56 g of uranium, 2.7 g of magnesium, and 200 ml of mercury.

Table 2.3 Solubility of Uranium in a
0.1 wt % Magnesium Amalgam

Temperature, °C	Reciprocal Temperature, 10 ³ /°K	Observed Solubility, wt %
356	1.59	1.41
356	1.59	1.43
300	1.74	0.912
270	1.84	0.640
175	2.23	0.217
125	2.51	0.0840
20	3.41	0.0056
75	2.87	0.0260
225	2.01	0.400
275	1.82	0.654
325	1.67	1.09
356	1.59	1.39

2.2 Solubility of Uranium and Thorium in the Same Mercury Solution

The solubility of uranium and thorium were found to be mutually depressed by the presence of the other in the same mercury solution (Table 2.4, Fig. 2.2). In a solution saturated with both uranium and thorium mercurides, the uranium concentration was essentially the same as its solubility in mercury alone at 356°C (1.20 wt %) while at 50°C it was lower by a factor of 4 (0.00215 wt %). Thorium concentration in the same solution was lowered by a factor of 2 from its solubility in mercury alone over the entire temperature

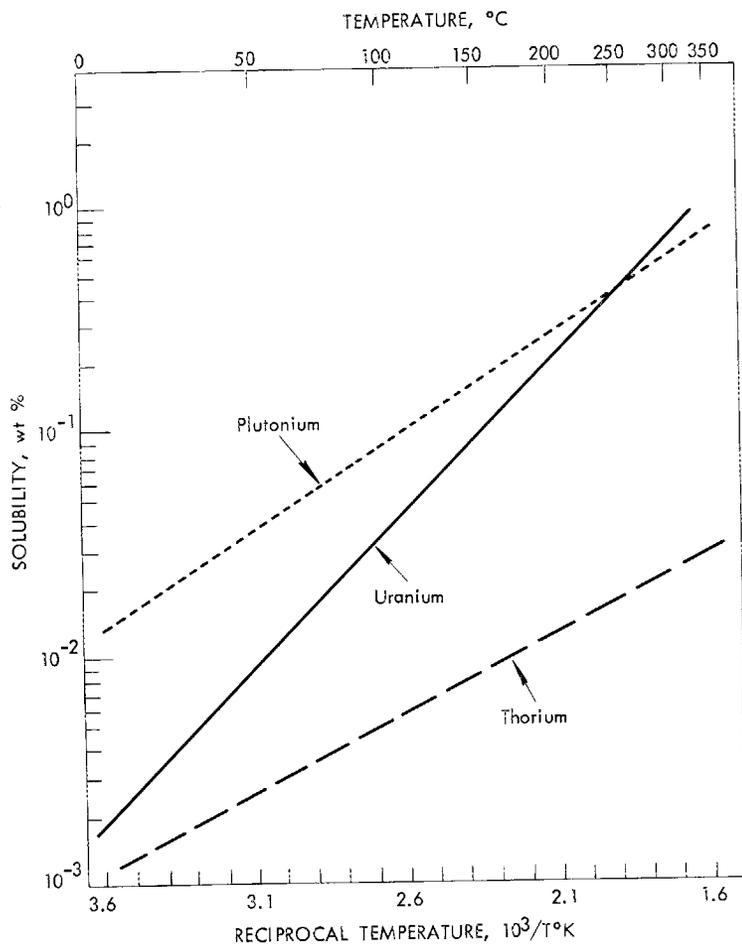


Fig. 2.1. Solubility of plutonium, uranium, and thorium in mercury. Plutonium from data of Bowersox and Leary.¹³

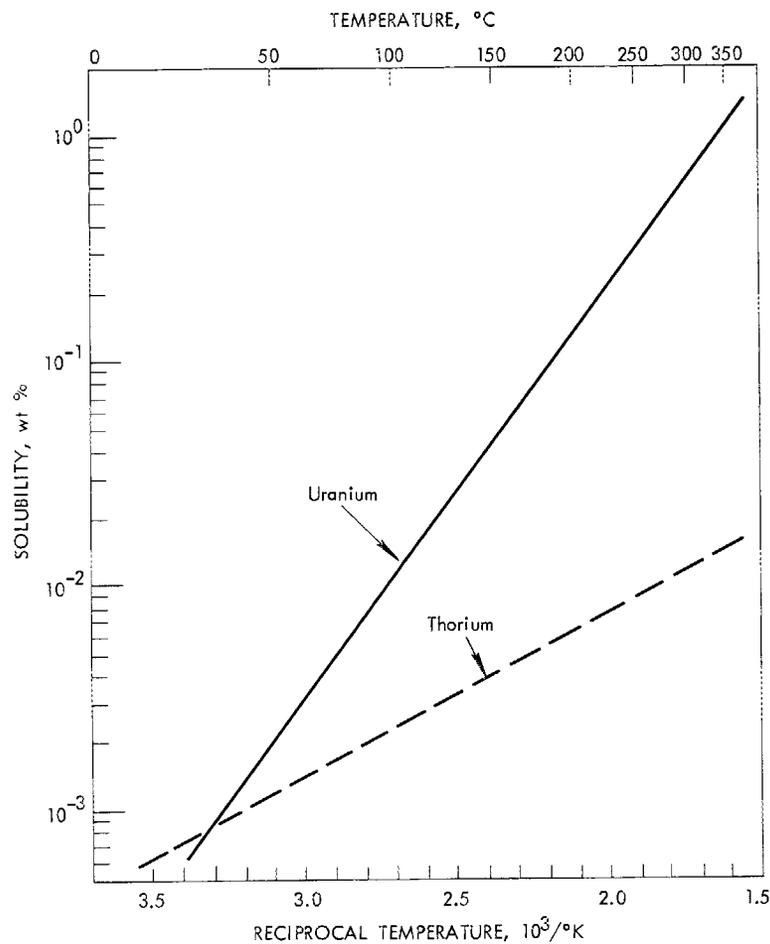


Fig. 2.2. Solubility of uranium and thorium in a mutually saturated solution.

range 50-356°C. The initial mixture was prepared by boiling 51 g of uranium and 22 g of thorium in 200 ml of mercury. Excess mercurides of both metals were present at all times. Results as reported are the averages of duplicate samples.

Table 2.4 Solubility of Uranium and Thorium in a Mutually Saturated Mercury Solution

Temperature, °C	Reciprocal Temperature, 10 ³ /°K	Solubility, wt % ^a	
		Uranium	Thorium
300	1.74	0.770	0.0118
200	2.11	0.155	0.00658
100	2.68	0.0124	0.00244
150	2.37	0.0475	0.00413
250	1.91	0.417	0.00968

^aAverage values of duplicate samples.

Thorium solubility in a solution containing a U/Th ratio equivalent to 4500 g of uranium per metric ton of thorium was essentially as observed in the complete absence of uranium. The quantity of uranium present was far below its solubility in mercury or in thorium-saturated mercury. Its concentration was therefore expected to remain constant at 0.0085 wt % over the entire temperature range investigated. Actually, the uranium concentration was observed to decrease from 1.91×10^{-3} to 8.8×10^{-5} wt % with a temperature decrease from 356 to 50°C (Table 2.5, Fig. 2.3). This unexpected result and the decreased solubility of uranium and thorium in the mutually saturated solution is thought to be due to coprecipitation of the mercurides, which is considerably pronounced in the case of a metal present in low concentration. The original system contained 51 g of thorium, 0.23 g of uranium, and 200 ml of mercury.

Two experiments were performed in which a mercury extraction of uranium from thorium was attempted. One extraction was from a mixture of the metals, the other from an alloy containing 4500 g of uranium per metric ton of thorium. Uranium concentration factors were about 50 and 6, respectively (Table 2.6). In the first extraction experiment, a 53-g mixture of 4500 g of uranium per metric ton of thorium was boiled in 200 ml of mercury. The hot solution was filtered, cooled to 50°C, and filtered again to remove the mercurides. The uranium/thorium ratio in the mercuride product was 0.22, corresponding to a uranium concentration factor of 50. In the second experiment, extraction of a 50-g sample of an alloy containing 4500 g of uranium per metric ton of thorium gave a mercuride product in which the uranium/thorium

Table 2.5 Solubility of a Uranium-Thorium Mixture in Mercury

U-Th: 50 g of mixture, 4500 g of uranium per metric ton of thorium

Hg: 200 ml

Temperature, °C	Reciprocal Temperature, 10 ³ /°K	Solubility, wt % ^a	
		Uranium	Thorium
353	1.60	0.00191	0.0278
200	2.11	0.000616	0.00922
50	3.09	0.000088	0.00214
125	2.51	0.000240	0.00574
275	1.82	0.00122	0.0191

^aAverage value from duplicate samples.

ratio was 0.027, a factor of 6 increase over the original ratio. Uranium and thorium concentrations in the mercury filtrates were approximately 1.3×10^{-4} and 2.8×10^{-3} wt %, respectively, in agreement with the solubility study of the 4500 g uranium per metric ton thorium mixture reported above (Fig. 2.3).

Table 2.6 Extraction of Uranium from Thorium

Samples containing 4500 g of uranium per ton of thorium extracted by 200 ml of mercury

	U/Th Ratio		U Con- centration Factor ^b	Concentration in Mercury after Filtration at 50°C, wt %	
	Sample	Product ^a		Uranium	Thorium
Mixture (53 g)	0.0044	0.22	50	1.3×10^{-4}	2.8×10^{-3}
Alloy (50 g)	0.0044	0.027	6	1.5×10^{-4}	2.8×10^{-3}

^aMixture was completely disintegrated, alloy only about 60%.

^bUranium concentration factor = $\frac{\text{U/Th ratio in product}}{\text{U/Th ratio in sample}}$;

Although the quantity of mercury used in the extraction experiments was sufficient to dissolve only 1 g of the thorium, the mixture was completely disintegrated and the alloy 60% disintegrated by the action of the boiling mercury. Insufficient time was allowed for complete disintegration of the alloy. The volume of thorium-saturated solution was 100 times the amount required to dissolve all the uranium. It was thought that the process would be one of progressive dissolution of the metals and crystallization of thorium after saturation had been reached. On filtration of the hot solution to remove solid phases, about 80% of the uranium was held by the excess thorium mercuride crystals. Because of the affinity of thorium for uranium, separations by dissolution in mercury are thought to be impractical.

2.3 Solubility of Rare Earth Metals in Mercury

Three rare earth representatives—gadolinium, samarium, and neodymium—were selected for solubility determinations because of their high fission yield and their significantly high thermal neutron capture cross section.¹⁸ In addition, because of the varying degree of completeness in the 4f subshell, each metal represents a sub-class within the rare earth series.

Application of the method of least squares to the observed solubility data (Tables 2.7-2.9) gave the following equations, together with their respective standard errors of fit:

$$\log \text{ of gadolinium solubility (wt \%)} = 1.83770 - 1222.01/T, \sigma_{\text{fit}} = 0.03539$$

$$\log \text{ of samarium solubility (wt \%)} = 1.41450 - 1036.45/T, \sigma_{\text{fit}} = 0.07606$$

$$\log \text{ of neodymium solubility (wt \%)} = 1.65023 - 1163.16/T, \sigma_{\text{fit}} = 0.1063$$

The solubilities of the three rare earth metals in mercury corrected according to these equations vary from 0.00895 to 0.785 wt % for gadolinium (Table 2.7, Fig. 2.4), 0.0131 to 0.585 wt % for samarium (Table 2.8, Fig. 2.4), and 0.00898 to 0.632 wt % for neodymium (Table 2.9, Fig. 2.4) between the temperatures 40 and 356°C. Calculated heats of solution are 5.59 kcal per mole of gadolinium, 4.74 kcal per mole of samarium, and 5.36 kcal per mole of neodymium.

The solubility of gadolinium was determined from the results of a single run in which initially 18 g was boiled in 100 ml of mercury. For samarium the data of two runs using 10.9 g and 20.0 g of samarium in 75 ml and 100 ml of mercury, respectively, were used. Two runs were also used in the neodymium solubility determination. In the first 13.6 g of neodymium and 75 ml of mercury were initially present while 20.7 g of neodymium and 100 ml of mercury were used in the second.

The removal of samples from the flask used up most of the reaction volume; however, some rare earth quasi amalgam and mercury always remained. Investigation of the residue always showed slight to moderate oxidation of

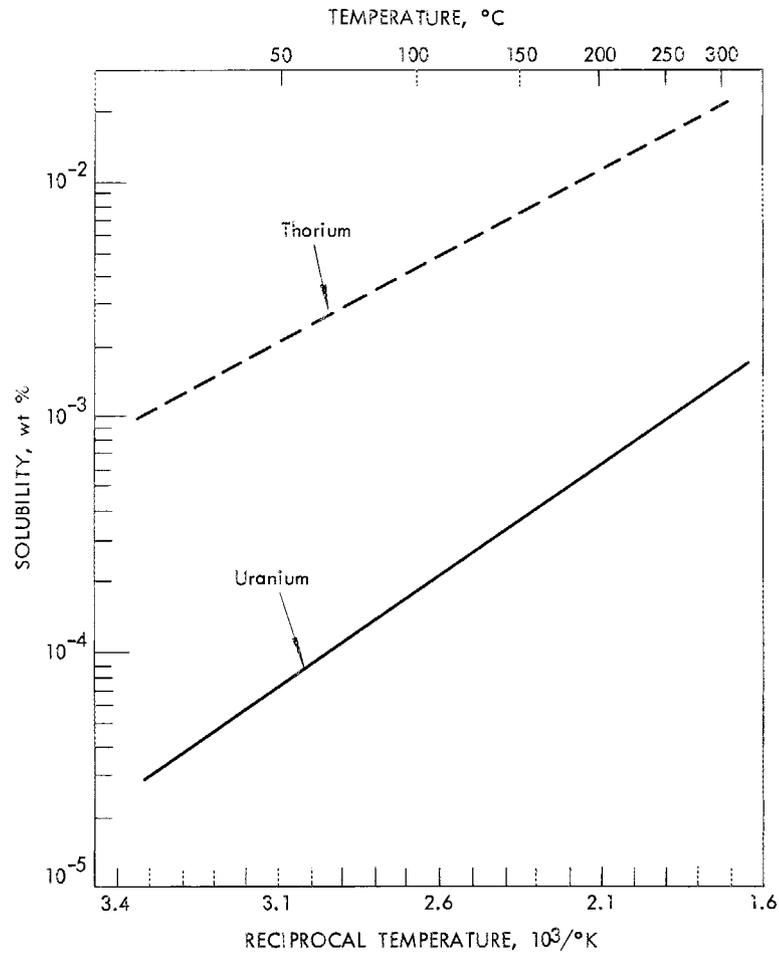


Fig. 2.3. Solubility of a uranium-thorium mixture, 4000 g of uranium per ton of thorium.

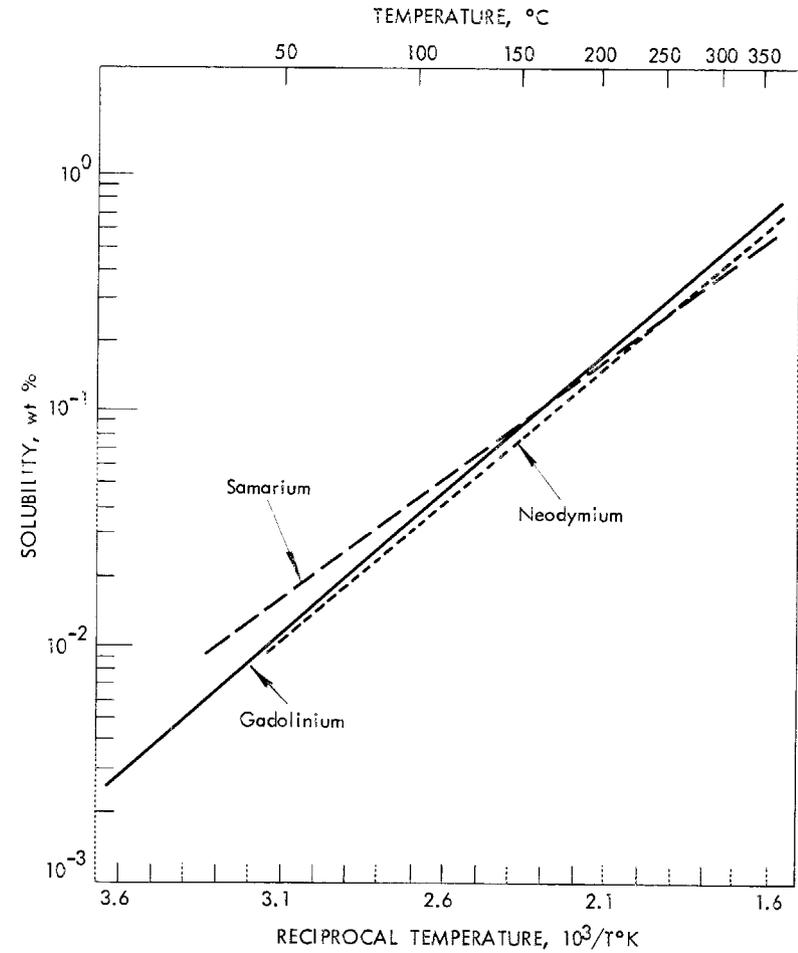


Fig. 2.4. Solubility of samarium, neodymium, and gadolinium in mercury.

Table 2.7 Solubility of Gadolinium in Mercury

Temperature, °C	Reciprocal Temperature, 10 ³ /°K	Solubility, wt %	
		Observed	Calculated ^a
335-345	1.64-1.62	0.760	0.691
280-290	1.81-1.78	0.419	0.447
210-220	2.07-2.03	0.215	0.216
145-150	2.39-2.37	0.0948	0.0862
90-95	2.75-2.72	0.0296	0.0309
130-135	2.48-2.45	0.0635	0.0669
205-210	2.09-2.07	0.212	0.198
280-285	1.81-1.79	0.443	0.435
40	3.19	---	0.00895
356	1.59	---	0.785

^aFrom equation \log of gadolinium solubility (wt %) = $1.83770 - 1222.01/T$.

Table 2.8 Solubility of Samarium in Mercury

Run No.	Temperature, °C	Reciprocal Temperature, 10 ³ /°K	Solubility, wt %	
			Observed	Calculated ^a
1	300-305	1.74-1.71	0.490	0.423
	170-175	2.26-2.23	0.104	0.124
	85-90	2.79-2.75	0.0376	0.0350
	145-150	2.39-2.37	0.0834	0.0887
	225-230	2.01-1.99	0.213	0.222
	40	3.19	--	0.0131
2	356	1.59	0.618	0.585
	300-305	1.74-1.71	0.467	0.423
	160-165	2.31-2.28	0.142	0.109
	100-110	2.68-2.61	0.0627	0.470
	195-205	2.14-2.09	0.168	0.167
	250-255	1.91-1.87	0.202	0.286

^aFrom equation \log of samarium solubility (wt %) = $1.41450 - 1036.45/T$.

Table 2.9 Solubility of Neodymium in Mercury

Run No.	Temperature, °C	Reciprocal Temperature, 10 ³ /°K	Solubility, wt %	
			Observed	Calculated ^a
1	295-300	1.76-1.74	0.418	0.420
	248-250	1.92-1.91	0.262	0.254
	200-204	2.11-2.09	0.188	0.147
	95-100	2.72-2.68	0.0357	0.0323
	40	3.19	--	0.00898
2	210-215	2.07-2.05	0.193	0.180
	105-110	2.64-2.61	0.0296	0.0395
	160-165	2.31-2.28	0.0746	0.0957
	245-250	1.93-1.91	0.196	0.258
	356	1.59	--	0.632

^aFrom equation \log of neodymium solubility (wt %) = $1.65023 - 1163.16/T$.

the rare earth metal. With gadolinium and samarium, only a slight amount of oxide was observed on the mercury surface. However, above the residue level there was a series of slight ridges which were coated with a layer of oxide. With neodymium a complete crust was formed at approximately the original mercury level, and considerable oxidation was evident on the upper surface of the crust.

Agreement between the observed solubilities and those calculated from the solubility equations were generally good for gadolinium, the two samarium runs, and the first neodymium run where equilibrium was approached from above. In the second neodymium run equilibrium was approached from below and agreement between observed and calculated solubility was poor, i.e., observed values were low. Evidently a rare earth mercuride crust forms over the surface of the mercury solution. When the first sample is withdrawn for analysis the crust and solution become separated. This would not affect results if equilibrium was being approached from above. However, if equilibrium was being approached from below, an unsaturated solution would result. The degree of this unsaturation at the time of the next sampling would thus depend on the extent of contact of crust with solution or condensing mercury.

2.4 Solubility of Several Fission Product Metals in Uranium-saturated Mercury

The solubility of ruthenium in mercury saturated with uranium varied from 1.2×10^{-3} wt % at 50°C to 1.1×10^{-2} wt % at 356°C (Table 2.10 and 2.11, Fig. 2.5). Palladium solubility in the same temperature range was

Table 2.10 Solubility of Ruthenium in Mercury Saturated with Uranium

Temperature, °C	Temperature, 10 ³ /°K	Solubility, wt % x 10 ³	
		Ru	U
356	1.59	10.1	1190
307-322	1.72-1.68	8.56	831
207-225	2.08-2.01	5.22	310
145-154	2.39-2.34	3.42	110
110-120	2.61-2.54	2.77	50
96-105	2.71-2.64	2.26	34
158-173	2.32-2.24	2.95	122
259-273	1.88-1.83	7.45	540
323-339	1.68-1.63	10.3	1030

Table 2.11 Solubility of Several Fission Product Metals in Mercury Saturated with Uranium

Tempera- ture, °C	Reciprocal Temperature, 10 ³ /°K	Solubility, wt %				
		U	Ru	Pd	Zr	Mo
356	1.59	1.23	11.0x10 ⁻³	23.3x10 ⁻⁵	< 3.8x10 ⁻⁴	< 5.4x10 ⁻⁵
252-260	1.90-1.88	0.490	7.72x10 ⁻³	15.0x10 ⁻⁵	< 1.4x10 ⁻⁴	< 2.2x10 ⁻⁵
195-204	2.14-2.10	0.244	5.88x10 ⁻³	10.7x10 ⁻⁵	< 1.9x10 ⁻⁴	< 3.0x10 ⁻⁵
88-100	2.77-2.68	0.0236	2.17x10 ⁻³	3.78x10 ⁻⁵	< 1.7x10 ⁻⁴	< 2.5x10 ⁻⁵
145-155	2.39-2.33	0.0910	3.83x10 ⁻³	6.45x10 ⁻⁵	< 2.2x10 ⁻⁴	< 3.3x10 ⁻⁵
290-300	1.78-1.74	0.672	10.2x10 ⁻³	16.8x10 ⁻⁵	< 2.0x10 ⁻⁴	< 3.0x10 ⁻⁵

2.1×10^{-5} wt % to 2.4×10^{-4} wt % (Table 2.11, Fig. 2.5). Dean¹⁹ reported ruthenium solubility in mercury to be of the order of 10^{-7} wt % while Leary³ reported a value of $<10^{-5}$ wt % over the temperature range 25 to 356°C. Thus, ruthenium solubility is increased by the presence of the uranium by factors of 10^4 to 10^5 . The only information available on palladium indicates a room temperature solubility of 6×10^{-3} wt %, ⁷ indicating that palladium solubility is decreased by the presence of uranium.

The concentrations of zirconium and molybdenum in the solutions submitted for analysis were below the limit of detection by neutron activation. The upper solubility limit reported here is calculated from the neutron activation detection limit. For zirconium, the upper solubility limit at 50°C is $<8 \times 10^{-5}$ wt % while at 356°C the limit is $<3.5 \times 10^{-4}$ wt %. The corresponding limits for molybdenum are $<1.2 \times 10^{-5}$ wt % at 50°C and $<5.4 \times 10^{-5}$ wt % at 356°C (Table 2.11, Fig. 2.5). Leary³ reports a mercury solubility of 7×10^{-4} wt % for zirconium and $<7.5 \times 10^{-6}$ wt % for molybdenum. Irving and Russell⁸ reported a room temperature solubility for molybdenum of $<2 \times 10^{-5}$ wt %. All values are in general agreement with this study.

Ruthenium solubility in uranium-saturated mercury was determined in a solution prepared by boiling 48 g of a 2% ruthenium-98% uranium alloy in 200 ml of mercury. It was also determined in a solution prepared by boiling 100 g of a 7% fissium-93% uranium alloy in 200 ml of mercury. In both cases the ruthenium solubility was the same, within experimental error. The solubilities of palladium, zirconium, and molybdenum were determined by analysis of samples taken from the solution in which the fissium alloy was dissolved. Composition of the fissium alloy furnished by Argonne National Laboratory was 0.30% cerium, 3.35% molybdenum, 2.50% ruthenium, 0.26% palladium, 0.36% zirconium, 0.47% rhodium, and the remainder uranium. The presence of the above metals did not affect the solubility of the uranium.

3.0 EXPERIMENTAL

3.1 Equipment

All equipment (Fig. 3.1) used in this study was of stainless steel construction. A 3-in.-dia by 8-in.-deep flanged dissolver was fitted with a cover and provided with a steel O-ring seal. The cover had a 1/8-in. line for an argon inlet, a 1/2-in. water-cooled exhaust line which also served as a mercury reflux condenser, a thermowell, and a 1/2-in. line with a gate valve for materials addition and sampling. The top of the gate valve was fitted with a compression seal to prevent inleakage of air during sampling.

For sampling, two 3/8-in.-o.d. transfer tubes were used, each of sufficient length to extend from the dissolver bottom, through the inlet gate valve, and to a sample collector. The inside diameter of one tube

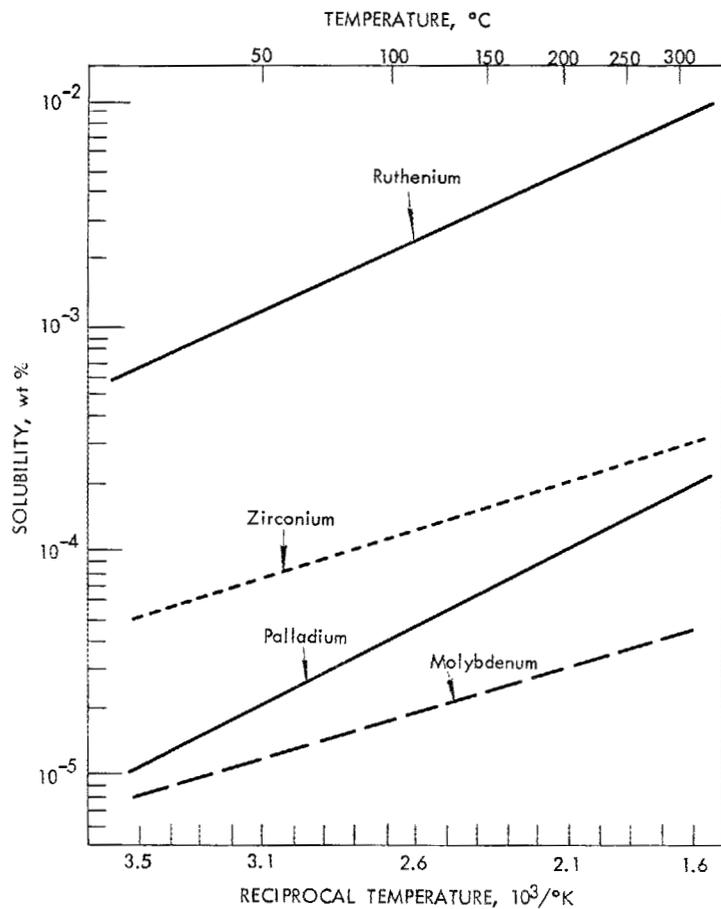


Fig. 2.5. Solubility of several fission product metals in uranium-saturated mercury. --- Established solubility; — upper solubility limit as defined by limit of detection.

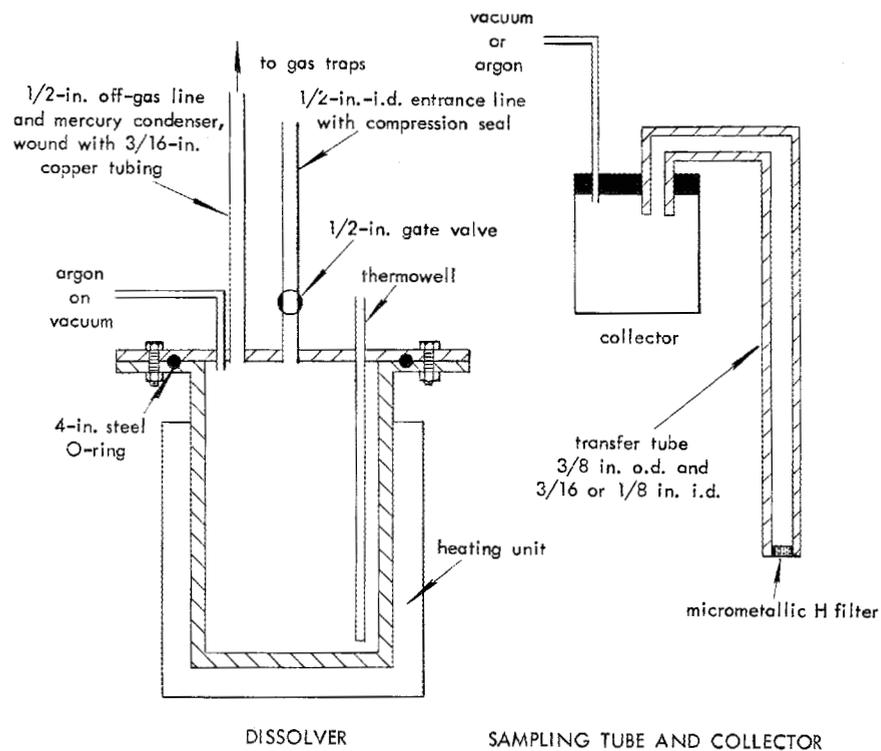


Fig. 3.1. Stainless steel apparatus for mercury solubility determinations.

was 1/8 in. and was used for temperatures of 200°C and below. For temperatures above 200°C, a 3/16-in.-i.d. tube was used. Argon or vacuum was supplied to the collector and transfer tube during sampling. A Micrometallic-G filter with an effective pore diameter of 3 μ was press-fitted into a 3/4-in.-long section which was screwed to the bottom of the transfer tube in use.

3.2 Preparation for a Solubility Determination

Prior to a run all equipment was cleaned with hot nitric acid, rinsed with distilled water, and dried with acetone followed by air. After assembly, the dissolver was outgassed by alternate evacuation to <100 μ Hg pressure followed by flushing with argon.

With the desired quantity of mercury added, usually 200 ml, the temperature was maintained at 150°C for approximately 12 hr to completely de-gas and dry both mercury and dissolver. A slow flow of argon was maintained over the mercury surface during this period and throughout the entire run.

The desired quantity of test material was introduced through the entrance valve. Air was excluded during the time the valve was open by temporarily increasing the argon flow. In order to assure equilibrium between the test sample and the mercury, several days of boiling was allowed prior to sampling. A similar equilibration period was allowed after each temperature change.

3.3 Sampling Procedure

Several difficulties were encountered during the sampling of the amalgam solutions. In general low results and inconsistent data were the result of these difficulties. The procedure finally adopted is described below.

Argon flow to the dissolver pot was increased to prevent leakage of air when the inlet gate valve was opened for the insertion of the transfer tube. Argon was also passed through the sample collector and transfer tube prior to and during the insertion of the tube in order to flush the air from inside. The inserted tube was suspended just above the mercury surface for 1/2 hr to heat it to the temperature of the amalgam. After the filter tip had been lowered below the surface and the argon flow through the tube discontinued, and additional 1/2 hr equilibration was allowed. Omission of the temperature equilibration resulted in crystallization of metal mercurides on and in the filter, plugging it or preventing transfer of part of the metal solute.

For transfer of solutions at or below 200°C, the 1/8-in.-i.d. tube was satisfactory. However, for solutions at temperatures above 200°C, mercuride was held up inside the tube unless a 3/16-in.-i.d. tube was used. In either case transfer proceeded smoothly when the length of tubing between the dissolver and sample collector was heated to a temperature somewhat above that of the sample taken. This was accomplished most simply by resistance heating.

Thus with the external section of the transfer tube heated to the appropriate temperature, the exhaust line was closed. A combination of argon pressure within the dissolver and vacuum applied to the collector and transfer tube forced mercury solution through the filter. With the first appearance of amalgam in the collector, the tube was withdrawn from the mercury solution and that which had passed the filter was forced over into the collector.

The 10-20 ml of amalgam collected was dissolved in nitric acid, combined with the internal washings of the transfer tube, and submitted for analysis for desired metal and mercury.

Samples containing ruthenium and palladium were treated differently. The mercury of the solution was dissolved in 8 N HNO₃ at a temperature below 60°C. The nitric acid solution was filtered through fine fritted glass to remove undissolved ruthenium and/or palladium, combined with aqueous washings of the residue, and submitted for analysis. The noble metal residue on the fritted glass was treated with 1 M NaOH--1 M NaOCl for 1 hr, in which time the ruthenium was completely dissolved. The alkaline solution was drawn through the filter and, if no palladium was present, acidified with nitric acid, and submitted for analysis. When palladium was present, it was dissolved in aqua regia, filtered, and combined with the alkaline ruthenium solution. No loss of ruthenium by volatilization was noted with this procedure.

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